UNIVERSITY
OF WOLLONGONG
AUSTRALIA

University of Wollongong
Research Online

Australian Institute for Innovative Materials - Papers

Australian Institute for Innovative Materials

2012

Isomorphism in Two (E)-1-(4-Halophenyl)-N-[1-(4-Methylphenyl)-1H-Imidazol-4-yl]Methanimines (Halide = Cl, Br)

Hanna Skrzypiec
Adam Mickiewicz University

Radoslaw Mazurek
The Silesian University of Technology

Pawel Wagner
University of Wollongong, pawel@uow.edu.au

Maciej Kubicki
Adam Mickiewicz University

Publication Details

Skrzypiec, H., Mazurek, R., Wagner, P. & Kubicki, M. (2012). Isomorphism in Two (E)-1-(4-Halophenyl)-N-[1-(4-Methylphenyl)-1H-Imidazol-4-yl]Methanimines (Halide = Cl, Br). Journal of Chemical Crystallography, 42 (10), 1036-1041.

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

Isomorphism in Two (E)-1-(4-Halophenyl)-N-[1-(4-Methylphenyl)-1H-Imidazol-4-yl]Methanimines (Halide = Cl, Br)

Abstract

The crystal structures of two imidazole-4-imines, (E)-1-(4-chlorophenyl)-N-[1-(4-methylphenyl)-1H-imidazol-4-yl]methanimine (1, C17H14ClN3), and (E)-1-(4-bromophenyl)-N-[1-(4-methylphenyl)-1H-imidazol-4-yl]methanimine, (2, C17H14BrN3), are isomorphous, the isostructurality index is 99.4 %. Both compounds crystallize in the triclinic space group P-1 with unit cell parameters at 100(1) K as follows: for (1), a = 7.9767(5) Å, b = 10.9517(7) Å, c = 16.6753(12) Å, α = 80.522(6)°, β = 87.046(6)°, γ = 89.207(5)°, and for (2), a = 8.0720(7) Å, b = 10.9334(10) Å, c = 16.8433(13) Å, α = 81.161(7)°, β = 86.605(7)°, γ = 89.505(7)°. The structures contain two symmetry—independent but conformationally similar molecules in the asymmetric unit (Z' = 2). In both compounds the overall twist of the molecule, defined as the dihedral angle between the terminal phenyl ring planes is significant, around 56°. The crystal packing is determined mainly be weak specific intermolecular interactions: the C–H···N hydrogen bonds connect molecules into infinite chains, and the chains are linked via C–H···X hydrogen bonds and by π–π interactions. This study illustrates the significant role of the weak interactions, which—in spite of their weakness—can robustly repeat in the crystal structures of similar compounds.

Keywords

cl, halide, imidazol, methanimines, br, yl, two, isomorphism, methylphenyl, n, halophenyl, 4, 1, e, 1h

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Skrzypiec, H., Mazurek, R., Wagner, P. & Kubicki, M. (2012). Isomorphism in Two (E)-1-(4-Halophenyl)-N-[1-(4-Methylphenyl)-1H-Imidazol-4-yl]Methanimines (Halide = Cl, Br). Journal of Chemical Crystallography, 42 (10), 1036-1041.

This journal article is available at Research Online: http://ro.uow.edu.au/aiimpapers/318

J Chem Crystallogr (2012) 42:1036–1041
DOI 10.1007/s10870-012-0354-1

ORIGINAL PAPER

Isomorphism in Two (*E*)-1-(4-Halophenyl)-*N*-[1-(4-Methylphenyl)-1*H*-Imidazol-4-yl]Methanimines (Halide = Cl, Br)

Hanna Skrzypiec · Radosław Mazurek · Paweł Wagner · Maciej Kubicki

Received: 14 February 2012 / Accepted: 4 August 2012 / Published online: 24 August 2012
© The Author(s) 2012. This article is published with open access at Springerlink.com

Abstract The crystal structures of two imidazole-4-imines, (*E*)-1-(4-chlorophenyl)-*N*-[1-(4-methylphenyl)-1*H*-imidazol-4-yl]methanimine (**1**, $C_{17}H_{14}ClN_3$), and (*E*)-1-(4-bromophenyl)-*N*-[1-(4-methylphenyl)-1*H*-imidazol-4-yl] methanimine, (**2**, $C_{17}H_{14}BrN_3$), are isomorphous, the isostructurality index is 99.4 %. Both compounds crystallize in the triclinic space group P-1 with unit cell parameters at 100(1) K as follows: for (**1**), a = 7.9767(5) Å, b = 10.9517(7) Å, c = 16.6753(12) Å, α = 80.522(6)°, β = 87.046(6)°, γ = 89.207(5)°, and for (**2**), a = 8.0720(7) Å, b = 10.9334(10) Å, c = 16.8433(13) Å, α = 81.161(7)°, β = 86.605(7)°, γ = 89.505(7)°. The structures contain two symmetry—independent but conformationally similar molecules in the asymmetric unit (Z' = 2). In both compounds the overall twist of the molecule, defined as the dihedral angle between the terminal phenyl ring planes is significant, around 56°. The crystal packing is determined mainly be weak specific intermolecular interactions: the C–H···N hydrogen bonds connect molecules into infinite chains, and the chains are linked via C–H···X hydrogen bonds and by π–π interactions. This study illustrates the significant role of the weak interactions, which—in spite of their weakness—can robustly repeat in the crystal structures of similar compounds.

Keywords Imidazole · Isostructuralism · Multiple molecules · Weak intermolecular interactions · Crystal structure

H. Skrzypiec · M. Kubicki (✉)
Department of Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland
e-mail: mkubicki@amu.edu.pl

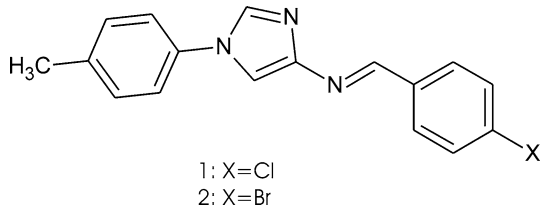
R. Mazurek
Institute of Organic Chemistry and Technology, The Silesian University of Technology, Krzywoustego 4, 44-100 Gliwice, Poland

P. Wagner
Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, University of Wollongong, Northfields Avenue, Wollongong, NSW 2522, Australia

Introduction

Nucleophilic substitution of the nitroimidazole system proved to be a versatile tool for modification of the imidazole moiety [1, 2]. The presence of the nitro group, essential for the reaction mentioned, becomes not only unnecessary but it can interfere with the next potential synthetic transformation. The reduction of the nitro group, relatively easy in benzene derivatives, has proven challenging in azole systems due to metastability of the resulting amines [3, 4]. To this end the reduction and further protection of the nitro functionality appears to be an important synthetic problem.

Quite interestingly it turned out that in the Cambridge Structural Database [5] there are only a few examples of 4-aminoimidazoles. Among those there is only one imine-derivative, ethyl 5-(4-methyl-3-phenyl-3H-thiazol-2-ylideneamino)-3-propyl-3*H*-imidazole-4-carboxylate [6], seven diaza-compounds (e.g., series of phenylazoimidazoles [7]), and one primary, six secondary, and 12 tertiary amines. During our studies on imidazole derivatives we have determined the structures of some imidazole-4-imines. Here we report the results of the analysis of two compounds (Scheme 1, Figs. 1, 2), namely (*E*)-1-(4-chlorophenyl)-*N*-[1-(4-methylphenyl)-1*H*-imidazol-4-yl]methanimine, (**1**),



Scheme 1 Chemical formulae for compounds **1** and **2**

and (*E*)-1-(4-bromophenyl)-*N*-[1-(4-methylphenyl)-1*H*-imidazol-4-yl]methanimine.

Results and Discussion

Compounds (**1**) and (**2**) are isostructural. It is possible to estimate the degree of isostructuralism using the descriptors introduced by Kálmán et al. [8] in his work on so-called "main-part" isostructuralism, or a more specific index defined by Kubicki and Szafrański [9]. The unit-cell similarity index is 0.01, very close to the ideal value of 0. Also the values of both isostructurality indices are close to the ideal values: according to [8] 99.3 % (ideal value 100 %), and according to [9] 0.985 (ideal value 1.0). The isostructuralism can be seen in the almost identical packing diagrams (Fig. 3).

Both compounds crystallize with two symmetry-independent molecules A and B in the asymmetric part of the unit cell. The results of the normal probability plot analysis [10, 11] for bond lengths and angles show that there are no

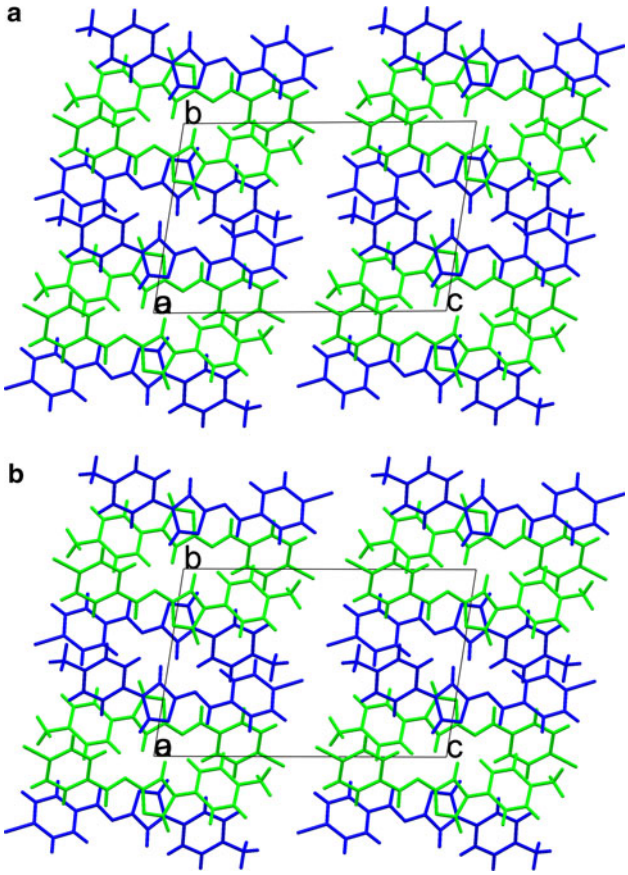


Fig. 3 Crystal packing of **a 1** and **b 2**, as seen along x-direction. *Different colors* denote symmetry-independent molecules (Color figure online)

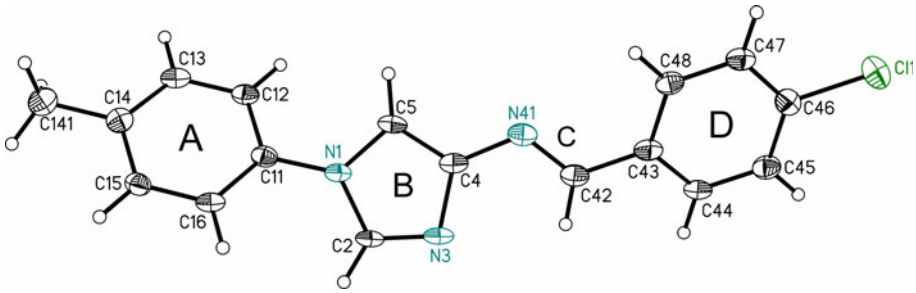


Fig. 1 Anisotropic ellipsoid representation of molecule **1**A together with atom labelling scheme. The ellipsoids are drawn at 50 % probability level, hydrogen atoms are depicted as *spheres* with arbitrary radii. Hydrogen bonds are drawn as *dashed lines*

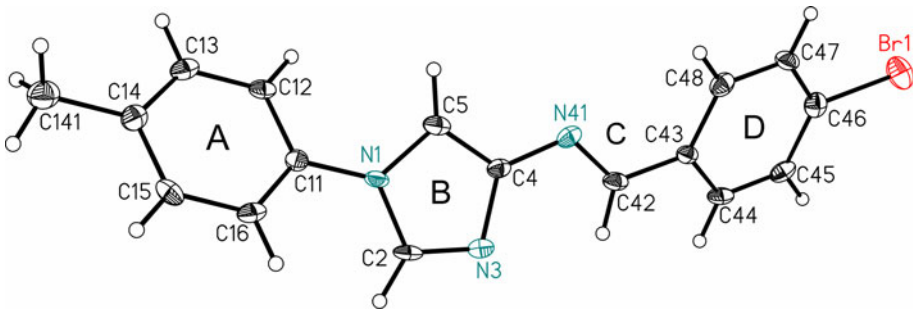


Fig. 2 Anisotropic ellipsoid representation of molecule **2**A together with atom labelling scheme. The ellipsoids are drawn at 50 % probability level, hydrogen atoms are depicted as *spheres* with arbitrary radii

Table 1 Selected geometrical data (Å, °) with su's in parentheses

	1A	1B	2A	2B
N1–C2	1.375(4)	1.375(4)	1.371(4)	1.371(4)
N1–C5	1.372(4)	1.374(4)	1.378(4)	1.380(4)
N1–C11	1.416(4)	1.415(4)	1.422(4)	1.421(4)
C2–N3	1.294(4)	1.305(4)	1.300(4)	1.306(4)
N3–C4	1.392(4)	1.391(4)	1.393(4)	1.392(4)
C4–N41	1.392(4)	1.381(5)	1.391(4)	1.393(4)
N41–C42	1.264(4)	1.273(4)	1.280(4)	1.273(4)
C42–C43	1.459(5)	1.457(5)	1.458(4)	1.466(4)
C46–Cl1(Br1)	1.737(3)	1.737(4)	1.899(3)	1.901(3)
C12–C11–C16	119.1(3)	119.2(3)	119.4(3)	119.9(3)
C13–C14–C15	117.1(3)	117.4(3)	117.0(3)	118.1(3)
C2–N3–C4	104.3(3)	104.6(3)	104.7(3)	104.3(3)
C4–N41–C42	119.0(3)	119.5(3)	118.6(3)	119.1(3)
N41–C42–C43	122.7(3)	121.6(3)	122.3(3)	120.7(3)
C44–C43–C48	118.6(3)	118.3(3)	118.5(3)	118.1(3)
C45–C46–C47	121.4(3)	120.8(3)	121.9(3)	121.6(3)
C5–N1–C11–C16	−147.9(3)	−147.9(3)	−147.7(3)	−148.8(3)
C5–N1–C11–C12	31.0(5)	31.1(5)	30.9(4)	30.8(4)
C5–C4–N41–C42	−170.0(3)	−169.9(3)	−169.4(3)	−168.8(3)
N3–C4–N41–C42	9.4(5)	9.5(5)	10.3(4)	9.7(4)
C4–N41–C42–C43	180.0(3)	178.4(3)	−179.7(3)	178.6(3)
N41–C42–C43–C44	−161.1(3)	−160.7(3)	−160.9(3)	−160.5(3)
N41–C42–C43–C48	18.0(5)	17.6(5)	17.5(4)	17.8(5)
A/B	31.30(14)	31.56(14)	31.28(12)	31.61(13)
B/C	9.7(2)	9.6(2)	10.6(2)	10.3(2)
C/D	18.5(4)	18.5(3)	18.6(3)	19.0(3)
A/D	55.79(9)	54.67(9)	56.44(8)	55.85(8)

Planes *A*, *B*, *C*, and *D* are defined in text and in Fig. 1

systematic differences between the molecules, and the actual differences are only of a statistical nature: R^2 correlation factors for bond lengths are 0.95 (**1**) and 0.97 (**2**), while for bond angles: 0.97(**1**) and 0.97(**2**).

Due to the isostructurality, the discussion can be made on one of the compound only (**1**), the geometrical values for the second one (**2**) will be given in square brackets.

The bond lengths and angles pattern is typical; the short N41–C42 bonds prove the double-bond character. The intra-annular bond angles within the phenyl rings reflect the nature of the substituents, generally in accordance with the findings of Domenicano and Murray-Rust [12] and Exner and Böhm [13].

The conformation of the molecule can be described by the dihedral angles between the subsequent planar fragments: methylphenyl group (*A*), imidazole ring (*B*), C−N C−C bridge (*C*) and halophenyl group (D). All these groups are essentially planar, maximum deviation from the least-squares plane is as small as 0.006(2) Å [0.013(3) Å]. The overall twist, defined as the dihedral angle between the terminal phenyl rings, is 55.79(9)° (56.44(8)°) in molecule A and 54.67(9)° (55.85(8)°) in molecule B. The values of the selected dihedral and torsion angles are listed in Table 1. It can be found that the 'sense' of the twists between the subsequent planes is the same, and the overall twist is roughly equal to the sum of the individual angles.

The crystal packing is determined mainly by the specific, directional weak interactions. The main motif, an ∼ABAB∼ chain along [010] direction, is created by relatively short and linear C5–H···N3 hydrogen bonds (Fig. 4; Table 2). In the high resolution structure of 1-phenyl-4-nitroimidazole [14] the topological analysis of the electron density distribution showed the critical points connected to the identical C5–H···N3 hydrogen bonds. The neighboring chains are connected along [101], the long axis of the molecule, by very weak C–H···X and C–H···π hydrogen bonds (Table 2; Fig. 5).

Experimental

Preparation of Compounds

1-(4-Methylphenyl)-4-nitroimidazole was reduced in a current of hydrogen under atmospheric pressure at room

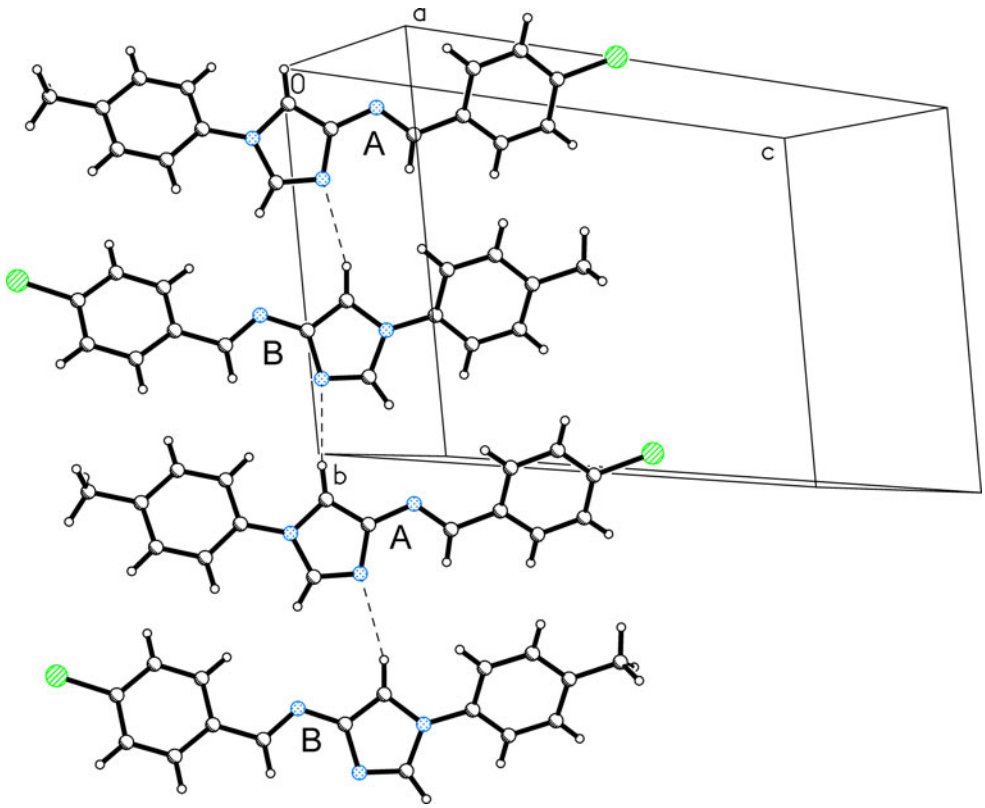


Fig. 4 The ~ABAB~ chain of the crystal structures, in the case of **1**. Hydrogen bonds are drawn as *dashed lines*

Table 2 Intermolecular interaction data (Å, °) with su's in parentheses

1						
D	H	A	D–X	H···A	D···A	D–H···A
C5A	H5A	N3B[a]	0.95	2.40	3.342(4)	173
C5B	H5B	N3A[b]	0.95	2.49	3.415(4)	164
C141	H14A	Cl1A[c]	0.98	3.07	3.830(4)	135
C142	H14F	Cl1B[d]	0.98	3.06	3.567(4)	113
C141	H14C	CgDA[e]	0.98	2.96	3.901(5)	160
C44A	H44A	CgAA[f]	0.95	2.81	3.558(4)	137
C16B	H16B	CgDB[f]	0.95	2.78	3.475(4)	130
C47B	H47B	CgAB[g]	0.95	2.77	3.456(5)	130
2						
D	H	A	D–X	H···A	D···A	D–H···A
C5A	H5A	N3B[a]	0.95	2.38	3.327(4)	173
C5B	H5B	N3A[b]	0.95	2.48	3.407(4)	165
C141	H14A	Br1A[c]	0.98	3.20	3.870(3)	127
C142	H14F	Br1B[d]	0.98	3.09	3.590(3)	113
C141	H14C	CgDA[e]	0.98	3.00	3.889(4)	152
C44A	H44A	CgAA[f]	0.95	2.82	3.581(4)	138
C16B	H16B	CgDB[f]	0.95	2.83	3.510(4)	130
C47B	H47B	CgAB[g]	0.95	2.76	3.459(4)	131

CgA and CgD denote middle point of rings A and D (cf. text); C141 and C142 are the methyl atoms from molecules A and B, respectively

Symmetry codes: [a]*x,−1 + y,−1 + z*; [b]*x,y,1 + z*; [c]*−1−x,−y,−z*; [d]*1 + x,y,1 + z*; [e]*−x,−y,−z*; [f]*−x,1−y,1−z*; [g]*−x,1−y,2−z*

temperature in methanol as a solvent. Freshly prepared Raney nickel was used as a catalyst. The TLC analysis showed that the starting material was consumed within an hour giving an undefined intermediate. The reaction was carried out until the entire intermediate compound was reacted out—usually 6 h. After filtering off the metal catalyst, because of its reactivity [2, 3], the resulting amine, was not worked out but immediately treated with aromatic

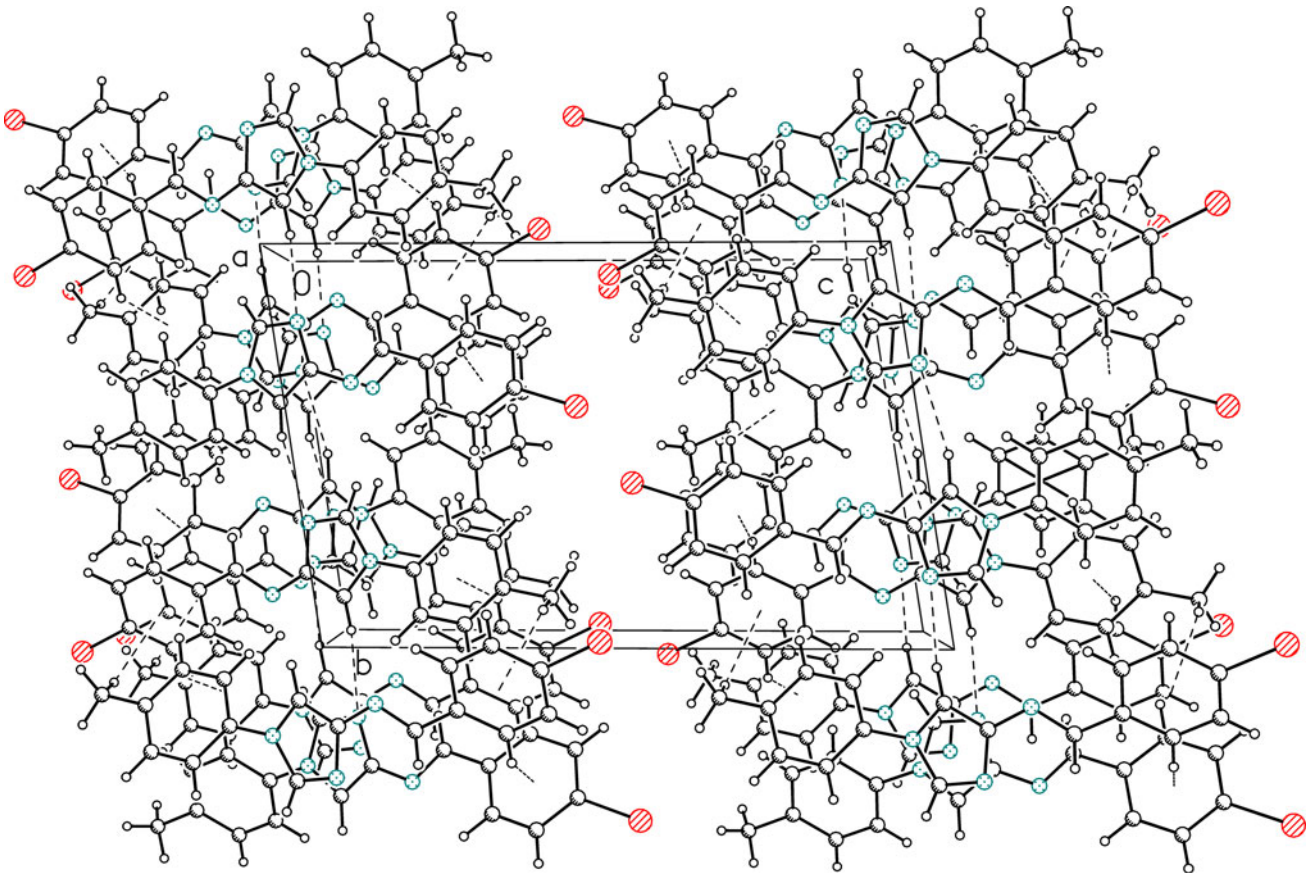


Fig. 5 The molecules of **2**, connected by weak interactions that involve π electrons (see text for details). The interactions are drawn as *dashed lines*

Table 3 Crystal data, data collection and structure refinement

Compound	**1**	**2**
Formula	$C_{17}H_{14}ClN_3$	$C_{17}H_{14}BrN_3$
Formula weight	295.76	340.22/c
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a(Å)	7.9767(5)	8.0720(7)
b(Å)	10.9517(7)	10.9334(10)
c(Å)	16.6753(12)	16.8433(13)
α(°)	80.522(6)	81.161(7)
β(°)	87.046(6)	86.605(7)
γ(°)	89.207(5)	89.505(7)
V(Å^3)	1,434.91(16)	1,466.3(2)
Z	4	4
d_x(g cm^{-3})	1.367	1.541
F(000)	616	688
μ (mm^{-1})	0.26	2.80
Θ range (°)	2.08–25.00	2.08–25.00
hkl range	$-9 \le h \le 9$	$-9 \le h \le 9$
	$-13 \le k \le 12$	$-13 \le k \le 12$
	$-19 \le l \le 19$	$-20 \le l \le 20$

Table 3 continued

Compound	**1**	**2**
Reflections:		
Collected	14,462	21,242
Unique (R_{int})	5,042 (0.046)	5,151 (0.047)
With I > 2σ(I)	3,930	4,226
No. of parameters	379	381
Weighting scheme:		
A	0.0696	0.0413
B	1.7884	1.1021
$R(F)$ [I > 2σ(I)]	0.069	0.038
w$R(F^2)$ [I > 2σ(I)]	0.164	0.086
$R(F)$ (all data)	0.091	0.051
w$R(F^2)$ (all data)	0.173	0.091
Goodness of fit	1.11	1.05
Max/min $\Delta\rho$ (e Å^{-3})	0.43/−0.50	0.65/−0.51

aldehydes. The addition of a catalytic amount of acetic acid caused the precipitation of the corresponding Schiff's bases in good yields.

Crystallography

Diffraction data were collected at 100(1) K by the ω-scan technique on an Agilent Xcalibur CCD-detector diffractometer with Sapphire detector and using graphite-monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz-polarization as well as for absorption effects [15]. Accurate unit-cell parameters were determined by a least-squares fit of 3,746 (**1**) and 5,533 (**2**) reflections of highest intensity, chosen from the whole experiment. The structures were solved with SIR92 [16] and refined with the full-matrix least-squares procedure on F^2 by SHELXL97 [17]. Scattering factors incorporated in SHELXL97 were used. The function $\Sigma w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o)^2 + (A \cdot P)^2 + B \cdot P]$ ($P = (\max(F_o^2, 0) + 2F_c^2)/3$). The final values of A and B are listed in Table 1. Anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. The hydrogen atoms were placed in geometrically idealized positions, and refined as rigid groups with their U_{iso}'s as 1.2 or 1.5 (methyl) times U_{eq} of the appropriate carrier atom. Programs XP [17] and Mercury [18] were used for graphic representations, used in Figures. Relevant crystal data are listed in Table 3, together with refinement details.

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC-866146 (**1**) and CCDC- 866147 (**2**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, e-mail:deposit@ccdc.cam.ac.uk, or www: www.ccdc.cam.ac.uk.

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

References

1. Swierczek K (1996) PhD Thesis, Silesian University of Technology, Gliwice
2. Wagner P (1999) PhD Thesis, Silesian University of Technology, Gliwice
3. Suwinski J, Walczak K (1994) Pol J Chem 68:675
4. Suwinski J, Wagner P (2000) Pol J Appl Chem 44:31
5. Allen FH (2002) Acta Crystallogr B58:380
6. Eltsov OS, Mokrushin VS, Rybalova TV, Gatilov YuV, Tkachev AV (2000) Mendeleev Commun 10:233
7. Anulewicz R, Maciejewska D (1996) Pol J Chem 70:742
8. Kálmán A, Argay G, Scharfenberg-Pfeifer D, Höhne E, Ribár B (1991) Acta Crystallogr B47:68
9. Kubicki M, Szafrański M (1998) J Mol Struct 446:1
10. Ibers JA, Hamilton WC (eds) (1974) International tables for X-ray crystallography, vol IV. Kluwer, Dodrecht, p 293
11. Abrahams SC, Keve ET (1971) Acta Crystallogr A27:157
12. Domenicano A, Murray-Rust P (1979) Tetrahedron Lett 24:2283
13. Exner O, Böhm S (2002) Acta Crystallogr B58:877
14. Kubicki M, Borowiak T, Dutkiewicz G, Souhassou M, Jelsch C, Lecomte C (2002) J Phys Chem B106:3706
15. Agilent (2010) CrysAlis PRO. Agilent Technologies, Yarnton
16. Altomare A, Cascarano G, Giacovazzo C, Guagliardi A (1993) J Appl Crystallogr 26:343
17. Sheldrick GM (2008) Acta Crystallogr A64:112
18. Macrae CF, Bruno IJ, Chisholm JA, Edgington PR, McCabe P, Pidcock E, Rodriguez-Monge L, Taylor R, van de Streek J, Wood PA (2008) J Appl Crystallogr 41:466